

# C E M E N T

AND

## CEMENT MANUFACTURE

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### Portland Cement Research.

A PAMPHLET\* recently issued by the Building Research Station gives what seem to be the preliminary results of an investigation of the behaviour of Portland cement when it is aerated to an excessive degree. The aeration is carried to the extent of rendering the cement entirely useless. As aeration is a dual process of attack by moisture and carbonic acid, the effect of these influences was studied separately in some preliminary experiments, which showed that dry carbon dioxide is entirely without effect on Portland cement. The pamphlet deals with the effect of excessive carbonation of unhydrated Portland cement. On first consideration the reader wonders why time has been spent on such an investigation, but in the end it will probably be admitted that the results obtained justify the labour.

In the major experiments a mixture of 70 per cent. moisture-saturated air and 30 per cent. carbonic acid was used as the carbonating medium. The experiments were made with three ordinary Portland cements and one rapid-hardening Portland cement. It is surprising to find one of the ordinary cements chosen for this work had a lime ratio, as calculated by the British Standard Specification, exceeding the limit allowed by that specification, and was in fact hardly distinguishable in strength from the rapid-hardening Portland cement used in the experiments. The amount of carbon dioxide absorbed by these cements was almost directly proportional to the time of exposure (which were periods up to thirty days) until a certain critical carbon dioxide content was attained; beyond this point the rate of absorption decreased. The carbon dioxide content at the critical point mentioned is constant for one cement but varies with different cements.

\* Building Research Technical Paper, No. 19. The Carbonation of Unhydrated Portland Cement. Price 1s. H.M. Stationery Office.

The strengths of the cements have been related to the degree of carbonation, and it is found that at early ages the neat strength first decreases linearly with carbonation until a critical value is reached beyond which further aeration has no effect until a second carbonate content is reached, after which strength falls to zero. Mortar strengths, however, differ strikingly from neat strengths in that initially increasing carbonation produces no effect on mortar strength and mortar strength is maintained at a higher degree of aeration than is the case with neat cement, i.e., mortar develops strength after the neat cement has lost the power to develop strength.

The relation between heat evolution both of the Portland cements and of tricalcium aluminate and tricalcium silicate has also been the subject of experiments, from which it is concluded that the main reaction occurring during early aeration is the decomposition of tricalcium aluminate, while during the later stages tricalcium silicate is chiefly involved. Comparing the rate of attack of aeration or carbonation on the tricalcium aluminate and tricalcium silicate it is obvious that the former is the first to be affected by carbonation, and this in turn influences the early strength of the cement.

The general conclusion is reached that for early ages the tricalcium aluminate exercises a predominant influence on the strength of cement, while at later ages this compound has little or no influence. This conclusion has already been accepted as a fact by those who have made synthetic cements and, indeed, by cement manufacturers generally, but it is interesting to find that it is supported in this somewhat roundabout fashion. If carbonation first attacks tricalcium aluminate, obviously the early development of the cement will be impeded; but as during this initial attack by carbonation the tricalcium silicate is untouched, then the later strengths of the cement will be unaffected. Continued carbonation will, of course, attack tricalcium silicate and reduce even the later strengths.

The somewhat naive statement is made that the investigation "shows quite conclusively that the possibility of the importance of tricalcium aluminate to the strength of Portland cement at early ages should not be overlooked in investigations concerning the hydraulic properties of these cements."

Investigations have been made upon the effect of carbonation on the setting-time of Portland cement, and the well-known effect of acceleration of the set is observed together with the unexplained phenomenon of the more aerated cement requiring a higher proportion of water to attain normal consistency. There are, however, certain fluctuations in the setting-time of the carbonated cement, that is to say, the setting-time does not regularly decrease with the absorption of carbon dioxide, and the theory is advanced that the cement particles may acquire a film of calcium carbonate which will decrease their activity and so prolong setting-time. With further aeration, it is suggested, moisture may penetrate this carbonate film causing further hydration of the core of the particle and even breaking off the film, thus exposing a fresh cement surface capable of quickening the set. This theory was supported by an experiment in which the carbonated cement which had become slow setting was gently rubbed with a rubber pestle in such a manner as might remove the carbonate film on the

particles; the effect then was to decrease the setting-time in a very marked degree.

The fact that cement subjected to intensive carbonation lost its neat strength long before it lost its mortar strength needed further investigation, and an ingenious theory is advanced that in the neat cement paste the few remaining active particles are, in effect, lost among inert completely-carbonated particles and thus cohesion becomes impossible; whereas in a mortar the grains of the sand act as links between the few active cement particles which are distributed over their surfaces and strength results because there is adherence between cement and rigid sand particles. Various experiments were made, the results of which supported this theory. On the other hand, there is a possibility, not referred to in the pamphlet, that the strength developed by the mortar may be due to the removal of the carbonate films on the cement particles by abrasion when sand and cement are mixed and thus the active cement particles are exposed and can exercise their strength.

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**The Hydrolytic Equilibrium of Calcium Aluminates.** By E. Peter von Polheim. (*Zement*, 1935, pp. 643, 659, 677.)—The behaviour of hydrated calcium aluminates in contact with lime water has been studied at temperatures between 20 deg. C. and 40 deg. C., and the following results obtained:

At a temperature of 20 deg. C. three calcium aluminates of different lime contents can exist in equilibrium with one another and with lime water if the lime and alumina contents of the solution correspond to the equilibrium conditions. Corresponding to the three hydrated compounds there are three stages in the lime-water concentration at which the precipitate, consisting of two solid phases (aluminium hydroxide + hydrated dicalcium aluminate, hydrated dicalcium aluminate + hydrated tricalcium aluminate, hydrated tricalcium aluminate + hydrated tetracalcium aluminate) exists in equilibrium with the solution.

The stability limits of hydrated dicalcium aluminate given by H. Kühl, F. Thilo, and A. Chi Yu were confirmed as being at 360 mg. CaO per litre and 109 mg.  $Al_2O_3$  per litre. The lower limit of stability of hydrated tricalcium aluminate is at 560 mg. CaO per litre and about 80 mg.  $Al_2O_3$  per litre. The lower limit of stability of hydrated tetracalcium aluminate is at 1,070 mg. CaO per litre and less than 3 mg.  $Al_2O_3$  per litre, and agrees with H. Lafuma's figures. All three hydrated calcium aluminates form hexagonal plates at 20 deg. C. Hydrated dicalcium aluminate forms very fine crystals which float in the liquid and give it a silky appearance; this can be taken as an indication of the presence of this substance.

At 37 deg. C. hydrated tricalcium aluminate takes the form of icosatetrahedra. Its field of stability lies between 360 mg. CaO per litre and saturated lime water. All hydrated calcium aluminates which are stable at 20 deg. change into this form of hydrated tricalcium aluminate at 37 deg. C.

## Effects of Fluorides on Thermal Combination of Portland Cement Mixtures.

By SHOICHIRO NAGAI and MASAMICHI TAKAHARA.

THE authors have issued a further report on their studies at the Imperial University of Tokyo on the effects of various fluorides on the thermal combination of Portland cement raw mixtures. A previous report was given in this journal for September, 1935.

In the latest report the effects of these fluorides on heating of various raw mixtures are compared as in the former report. An abstract of the paper is as follows:

Four kinds of raw mixture were obtained, one from the cement mill and the other three samples by the preparation in the laboratory from limestone, ganister, coal ash, pyrite cinder, and copper slag. The chemical compositions of these samples are shown in Table I.

TABLE I.

Mixture.	Loss on ignition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Total
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
RMA .. ..	19.15	19.24	2.99	1.02	55.77	1.29	99.46
RMB .. ..	35.22	14.28	4.14	2.14	43.21	0.94	99.93
RMC .. ..	34.75	14.71	4.45	2.14	42.47	0.73	99.25
RMD .. ..	32.41	13.84	3.53	5.94	42.02	1.36	99.10

Mixture RMA was a mixture composed of clay and insufficiently decomposed lime, so that the ignition loss is considerably smaller than the common mixture of limestone and clay. Mixture RMB was prepared from limestone, coal ash, and copper slag in the proportion of 74 : 13 : 13 with the object of using slag from copper refineries, and is a type of high-iron-oxide special Portland cement.

These raw mixtures were mixed with 0.5 and 1 per cent. of three fluorides CaF<sub>2</sub>, NaF and MgF<sub>2</sub>, and heated at 1,200 to 1,350 deg. C. for one hour. The loss on heating, the free lime and insoluble residue of the heated mass were analysed, and the results compared with mixtures heated without fluoride (Table 2). It is clearly seen that (1) NaF is most effective in the combination of raw mixture, (2) MgF<sub>2</sub> is not so effective as CaF<sub>2</sub>, (3) the effect of added fluoride on the combination between CaO and the acid components SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is most clearly seen by heating at 1,300 to 1,350 deg. C., owing to the formation of calcium silicates 3CaO.SiO<sub>2</sub> and 2CaO.SiO<sub>2</sub>, and (4), mixture RMD of high-ferric-oxide content combines completely even when heated at 1,300 to 1,350 deg. C. with a small amount of CaF<sub>2</sub>.

Next the effects of the addition of feldspar (f), glass (G), and a special mixture (M), which is a by-product of a calcium superphosphate fertilizer factory and composed principally of SiO<sub>2</sub> and NaF, were studied by using the raw mixture

TABLE 2.  
EFFECTS OF FLUORIDES ON HEATING RAW MIXTURES FOR ONE HOUR.

Mixture.	Temperature.	Fluoride		Loss on heating.	Free lime	Insoluble residue.	Residual fluoride	
		Kind	Amount of fluorine.				Amount of fluorine	Per cent.
(I) {	1200	—	(%)	(%)	(%)	(%)	(%)	(%)
		—	—	21.45	24.78	3.43	—	—
		CaF <sub>2</sub>	1.0	19.71	6.68	0.91	—	—
		NaF	1.0	21.54	6.25	0.18	—	—
(II) {	1300	—	—	19.03	11.43	0.39	—	—
		CaF <sub>2</sub>	0.5	19.40	4.60	0.20	0.13	21.0
		NaF	0.5	19.80	3.43	0.13	0.17	27.4
		MgF <sub>2</sub>	0.5	20.11	4.80	0.24	0.14	22.6
(III) {	1350	—	—	21.05	6.79	0.20	—	—
		CaF <sub>2</sub>	0.5	20.32	4.37	0.20	—	—
		NaF	0.5	20.53	3.42	0.15	—	—
		MgF <sub>2</sub>	0.5	21.45	4.54	0.18	—	—
(IV) {	1300	—	—	35.22	6.81	0.16	—	—
		CaF <sub>2</sub>	0.5	35.07	3.84	0.15	—	—
		—	—	35.09	6.35	0.11	—	—
		CaF <sub>2</sub>	0.5	35.15	0.31	0.15	—	—
(V) {	1300	—	—	32.45	3.25	0.18	—	—
		CaF <sub>2</sub>	0.5	33.59	0	0.19	—	—
		—	—	—	—	—	—	—
		CaF <sub>2</sub>	0.5	—	—	—	—	—

RMB and treating as previously and comparing it with the effect of CaF<sub>2</sub>. The results are shown in Table 3.

TABLE 3.  
EFFECTS OF VARIOUS ADMIXTURES ON HEATING RAW MIXTURE FOR ONE HOUR.

Mixture.	Temperature.	Admixture		Loss on heating.	Free lime.	Insoluble residue.
		Kind.	Amount.			
(VI) {	1300	—	(%)	(%)	(%)	(%)
		Glass	1	34.82	6.50	0.26
		Feldspar	1	34.80	5.89	0.27
		Special Mixture	1	34.89	2.89	0.10
(VII) {	1350	—	—	—	—	—
		Glass	3	34.21	2.22	0.13
		Feldspar	3	34.32	0.63	0.14
		Special Mixture	3	34.90	0.19	0.07
(VIII) {	1350	—	—	—	—	—
		Glass	2	34.76	1.80	0.35
		Feldspar	2	34.88	0.59	0.20
		Special Mixture	2	35.67	0.68	0.14
(IX) {	1300	—	—	—	—	—
		CaF <sub>2</sub>	0.5	35.07	3.84	0.15
		—	—	—	—	—
		CaF <sub>2</sub>	0.5	35.41	2.10	0.13
(IX) {	1350	—	—	—	—	—
		CaF <sub>2</sub>	1.0	35.50	1.26	0.10

A comparison of series (IX) using  $\text{CaF}_2$  with series (VI), (VII), and (VIII) shows that (1) the mixture obtained from the by-product from the superphosphate industry is most effective, owing to the content (about 25 per cent.) of effective NaF as shown in Table 2, (2) feldspar is rather more effective when added in amounts of 2 to 3 per cent. and heated at 1,300 to 1,350 deg. C. or over than a small amount of  $\text{CaF}_2$ , (3) glass of the soda-lime-silica type is not so effective as  $\text{CaF}_2$ .

The mixture containing about 25 per cent. NaF and about 58 per cent.  $\text{SiO}_2$  obtained from the calcium superphosphate fertiliser factory was again compared for its effect on the thermal combination of calcium silicates by adding 0.5 to 1 per cent. to the mixture  $3\text{CaCO}_3 : \text{SiO}_2$  or  $2\text{CaCO}_3 : \text{SiO}_2$  as already reported. The effect was proportional to the amount of NaF in the mixture, but the large content of silica (about 58 per cent.) in this mixture lowers the molecular ratio of combined lime to combined silica.

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## Manufacture of Aluminous Cement in Blast Furnaces.

In *Technische Blätter* (No. 25, 1935, p. 452), Dipl. Eng. E. Reitler discussed aluminous cement manufacture at some length. The following is abstracted from his remarks.

Experiments in the operation of blast-furnaces to yield a slag high in alumina have been made several times. In 1904 the Pennsylvania Steel Co. made experiments with the object of discovering a way to smelt Cuban (Mayari) iron ore which was of a highly aluminous character. This experiment was regarded as a failure because the coke consumption amounted to 2,130 kg. for each ton of pig iron produced; there was also a great amount of dusting in the furnace operation. In 1924 a further experiment was made with better results. The alumina content of the slag was about 30 per cent., and the silica content 20 to 25 per cent., while the furnace operation proceeded normally. The iron product was also normal. In 1927, Messrs. T. L. Joseph, S. P. Kinney, and C. E. Wood operated a blast-furnace and obtained a slag with about 49 per cent. alumina, 42 per cent. lime, 4 to 5 per cent. silica, and 1 per cent. ferrous oxide. The furnace had a useful capacity of only 16 cubic metres. The charge consisted of a mixture of bauxite, limestone, and iron ore low in silica, or iron scrap, or both. The desired composition of the slag was approximately reached, although the silica content was rather high. The iron product was regarded as a by-product, and amounted to 2.6 to 3.3 tons in twenty-four hours.

Similar results had been reached in Germany in large-scale experiments from 1925 to 1928 in the Lübeck works of the Rolandshütte in Weidenau. The operations were extended over considerable periods, the last being continued through August and September 1928. In this case it was sought to obtain both a normal quality pig iron, and an aluminous slag cement. The experimental furnace was built of rough masonry, with a normal internal profile; its capacity was 74 cubic



metres, and therefore corresponded to normal blast-furnace practice. The air blast, pre-heated to 550 deg. C., was delivered to the furnace through four separate points.

The process was reported in *Archiv f. das Eisenhüttenwesen* as follows: As carrier of the alumina in the first experimental period, bauxite of Hessian and Istrian origin was used; in the second period French bauxite was used, and in the third period chiefly Istrian bauxite. On the one hand to favour the output of iron, and on the other to keep the silica content of the slag as low as possible and thus improve its cement-making qualities, rolling-works sinter and some calcined pyrites were used in the first period; later, concentrated Krivoi-Rog iron ore and also scrap iron were added to the charge. The operations proceeded satisfactorily, but the coke consumption was rather high. The slag composition was maintained without difficulty at about 45 per cent. alumina, 42 per cent. lime, less than 10 per cent. silica, and 2 per cent. ferrous oxide, and the cement properties corresponded to expectations. The pig iron contained 4 to 5 per cent. carbon, 0.3 per cent. silicon, and a low sulphur content; it somewhat resembled high-carbon Swedish charcoal-iron, and generally showed a variegated but seldom an all grey or all white fracture.

These experiments showed that in ordinary blast-furnace operation it was possible to produce without difficulty a high-grade pig iron and a highly aluminous cement of good quality, and led to the continuance of the experiments over a period of two and a half months to test the economic results of the so-called "bauxite-process." Hessian and Istrian bauxites were used together, mixed with limestone and scrap iron, with coke as fuel. The iron scrap was 26 to 29 per cent. of the total charge. The desired composition of the pig iron was obtained without difficulty; it showed a grey fracture, or one chiefly grey but white in places, but rarely white with grey places. The composition of the slag, with a maximum of 7.5 per cent. silica, at least 45 per cent. alumina, and at the highest 40 per cent. lime, was within the desired limits, and in regard to silica content was particularly favourable; the ferrous oxide content amounted to 2 to 4 per cent. The slag product acquired a tensile strength under water of 35.3 kg. per square centimetre in 24 hours, and a crushing strength in the same time of 698 kg. per square centimetre. After 28 days under water these values had increased to 49.2 and 951 kg. per square centimetre respectively.

In general, the economy of blast-furnace operation is measured according to the coke consumption per ton of pig iron produced; the slag is a more or less undesired by-product, and the quantity is kept as low as possible. In the process described, in which the slag forms a high-grade product, the ascertained coke consumption, which was reduced from 1,400 kg. in the beginning to 800 kg. per ton of pig iron produced, is no absolute criterion of the economy of the process, but it can serve as a proof that the bauxite operation in blast-furnace practice, apart from the value of the slag, is a favourable one.

A large production in Germany of aluminous cement by this process is hampered by the necessity of importing bauxite at considerable cost.

## Cements for Special Purposes.

By R. ZOLLINGER.

It often happens that cements which have given high strengths in laboratory tests do not reach the same strengths in practice. Usually this result is due to the use of a cement which is not suitable for the particular purpose, although it may be good as a representative of its class.

There are several types of cement each good of its kind. It should be remembered that four different chemical constituents occur in cement in varying amounts, and the proportion of any constituent determines the suitability of the cement for a particular purpose. The strength values are only one aspect of the quality of a cement, and the chemical properties should be given more consideration.

There are six chemical factors which determine the value of a cement. The two first are the loss on ignition and the residue insoluble in a 10 per cent. hydrochloric acid solution. The raw materials of cement are more or less insoluble in hydrochloric acid, and show a high loss on ignition due to their carbon dioxide content. During burning, however, compounds are formed while the carbon dioxide is expelled, and these compounds are completely soluble in a 10 per cent. solution of hydrochloric acid. The quality of the cement is higher, therefore, as the loss on ignition and insoluble residue approach zero.

These chemical factors give an idea of the quality of the cement, but not of its type. In judging the type of a cement there are four values which are of great use. The first is the lime standard. Theoretically  $2.8 \times (\text{per cent. SiO}_2) + 1.18 \times (\text{per cent. Al}_2\text{O}_3) + 0.65 \times (\text{per cent. Fe}_2\text{O}_3)$  should give the lime content of the cement. In practice its value lies between 90 and 98 per cent. of the theoretical amount. The nearer this approaches 98 per cent. the greater will be the early strength and the ultimate strength. A lower lime content results in a decrease in strength, a lower shrinkage and heat of hydration, and a greater resistance to chemical attack. Therefore, according to the purpose for which it is required, a cement with lower strength may be more suitable than a cement with higher strength. If, nevertheless, a high strength is obtained, especially a high early strength, the proportion of silica according to the ratio of silica to alumina + iron oxide for cements with the same lime standard must be examined and the cement with the highest ratio chosen. Cements of this type are expensive since their manufacture requires a large coal consumption.

The ratio of alumina to iron oxide must also be considered. A high iron-oxide content with respect to the alumina content results in less shrinkage, less heat of hydration, and greater resistance to attack by corrosive liquids. These cements also have high early strength and are stable in sea water. Their only disadvantage is that they are seldom manufactured, since most raw materials are too low in iron oxide and require an addition of this constituent which is not always easily obtained. In addition these cements are not suitable for poured concrete and



grouting, as they are sensitive to large amounts of gauging water and suffer a large decrease in strength if a certain maximum is exceeded.

Professor Serban Solacolu of the Technical High School at Bukarest was the first to make a classification of these chemical data and has constructed a diagram based on it which is of great use to the cement user. In this diagram (*Fig. 1*) the ratio of silica to alumina + iron oxide (silica ratio) is used as ordinate and the ratio of alumina to iron oxide as abscissa. A continuous series of cements is

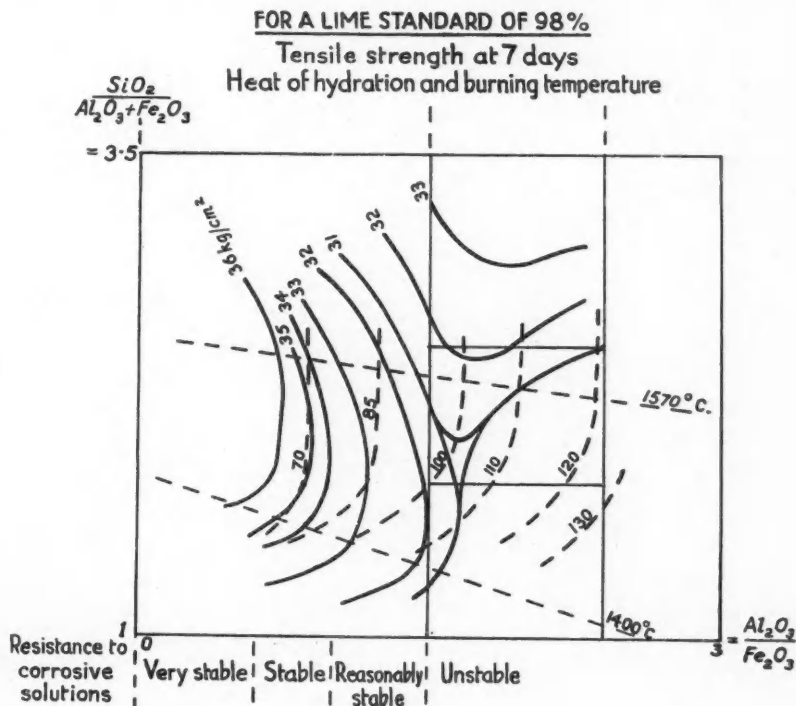


Fig. 1.

obtained with iron cements on the left (Brownmiller cement, Kühl cement, etc.), ordinary Portland cements in the middle, and aluminocements on the right. In the vertical direction there are cements low in silica at the bottom, normal cements in the middle, and high-silica cements at the top. The curves of strength at seven days and heat of hydration show the advantages possessed by iron cements. The resistance to chemical action also shows how the quality in this respect rises towards the left. The curves are referred to a lime standard of 98 per cent.; for a lime standard of 90 per cent. there is a correspondingly large decrease in strength which is greatest for the iron cements. Iron cements should

therefore always have a high lime standard ; this is safe since, compared with other types of cement, the heat of hydration, shrinkage, and chemical resistance can be guaranteed.

According to Professor Solacolu the following are the classes into which cements can be divided :

Iron cements : Alumina modulus less than 1.5. High early strength. Low heat of hydration and shrinkage. High resistance to corrosive liquids. Low sintering temperature. All these properties improve as the alumina modulus is reduced and hence iron cements are the best for road and sea-water construction.

Portland cements : Alumina modulus 1.5 to 2.4. These are best suited for mass concrete. With high silica content, i.e. when the silica ratio is greater than 2.5, they approach iron cements in their properties without quite attaining that standard. They are obtained only by high burning temperatures which make them expensive.

Alumino-Portland cements : These cements, with an alumina modulus greater than 2.5, have the advantage over Portland cement in that they are less sensitive to an excess of gauging water and are therefore suitable for poured concrete and grouting. As an example, they are eminently suitable for oil wells as they can be quickly worked up again.

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#### **Congress of the International Association for Testing Materials.—**

The second international congress of the International Association for Testing Materials will be held in London from April 19 to 24, 1937, under the presidency of Sir William Bragg, O.M., K.B.E. The subjects for discussion include concrete and reinforced concrete, erosion and corrosion of natural and artificial stone, methods of testing ceramic bodies, relation between the results of laboratory tests and behaviour in use and service, the bearing of recent advances in physics and chemistry on the knowledge of materials, and the properties of materials for the thermal and acoustic insulation of buildings. For further information enquiries should be addressed to the Honorary Secretary of the Congress (Mr. K. Headham-Morley), The International Association for Testing Materials, 28 Victoria Street, London, S.W.1.

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## The Carbonation of Unhydrated Portland Cement.

IN a Technical Paper (No. 19) of the Department of Scientific and Industrial Research, published by H.M. Stationery Office (price 1s.), Mr. D. G. R. Bonnell, M.Sc., Ph.D., discusses the effect of exposing cements to the action of carbon dioxide. The following is an abstract of the paper :

The investigation, which was carried out at the Building Research Station, comprised six separate studies, namely, (1) Preliminary experiments to isolate the factors chiefly responsible for the modification of the properties of cement brought about by aeration. (2) The variation of the rate of absorption of carbon dioxide by cement as aeration proceeds. (3) The relation between the state of carbonation and the tensile strength of the cement. (4) The effect of carbonation on the heat evolved by the cement on hydration in excess of water. (5) The effect of carbonation on the setting time of Portland cement. (6) The behaviour of aggregate in cement mortars. Four Portland cements, three normal and one rapid-hardening, were investigated ; the chemical analyses of these cements are given in Table I.

TABLE I.

	Portland cement.			Rapid-hardening Portland cement.
	A.	B.	C.	
SiO <sub>2</sub> .. .. .	22.3	18.88	21.86	21.08
Al <sub>2</sub> O <sub>3</sub> .. .. .	6.26	6.26	4.52	6.47
Fe <sub>2</sub> O <sub>3</sub> .. .. .	1.80	4.49	2.15	1.83
TiO <sub>2</sub> .. .. .	0.29	0.35	0.33	0.30
CaO .. .. .	65.6	65.1	65.60	65.45
MgO .. .. .	0.88	0.72	1.04	0.87
Na <sub>2</sub> O .. .. .	0.39	0.12	0.06	0.35
K <sub>2</sub> O .. .. .	0.58	0.43	0.73	0.60
SO <sub>3</sub> .. .. .	1.65	1.98	1.94	2.45
Loss on ignition .. .. .	0.92	1.93	—	1.55

To examine the effects of moisture and carbon dioxide on cement, samples of a typical normal Portland cement were exposed to atmospheres of (a) moisture-saturated air free from carbon dioxide ; (b) dry air with carbon dioxide ; (c) saturated carbon dioxide ; and (d) various mixtures of carbon dioxide and moisture-saturated air. The effects were studied by determining the carbonate content and the loss on ignition of the cement after various periods of exposure.

The apparatus used in these experiments is shown diagrammatically in Fig. 1.

About 800 grams of cement "C" (Table I) were placed in the glass tube A, fitted with inlet and outlet tubes  $T_1$  and  $T_2$ . By means of a two-way tube,  $T_1$  is joined to sources of moist air and carbon dioxide. To expose the sample to dry carbon dioxide, tap  $t_2$  is closed and wash bottle  $w_1$  removed from the circuit. When moist air is used  $t_1$  is closed and  $t_2$  opened. For mixtures of moist air and

carbon dioxide the drying tower *D* and the *KOH* towers are removed. At definite intervals during the exposure of the sample the tube *A* is closed at  $T_1$  and  $T_2$  and removed in order that the cement may be thoroughly stirred and mixed so as to ensure the continued exposure of fresh surfaces to the action of the particular atmosphere. Periodically after such mixing a sample was removed and the loss on ignition and the carbon dioxide content determined. The difference in these two values was assumed to be due to free and combined water.

The results showed that dry carbon dioxide has no effect on the cement, while with moist air (free from  $\text{CO}_2$ ) the change is very small. On the other hand, with mixtures of moist air and carbon dioxide the loss on ignition and the carbonate content increase very rapidly with increasing time of exposure. The increase in the water content with time is small but definite. All the experiments carried out on unaerated cements proved that dry carbon dioxide had no effect, but it was considered possible that such an atmosphere might influence a partially aerated sample, but even after previously exposing the cement to saturated  $\text{CO}_2$  until the loss on ignition was 7.76 per cent. all action ceased on changing over to a dry atmosphere.

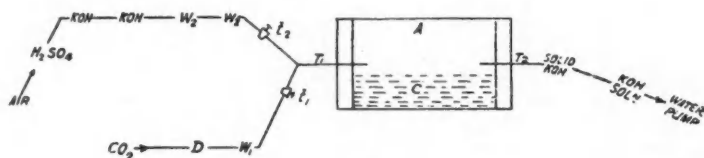


Fig. 1.

As a result of this preliminary work it was decided for the main investigation to aerate cement with a moisture-saturated mixture of air (70 per cent.) and carbon dioxide (30 per cent.). This was done as described above except that the tube *A* was replaced by a number of steel drums in each of which about  $\frac{3}{4}$  cwt. of cement could be treated. Once a day these drums were shaken and the cement thoroughly mixed.

Experiments were carried out to determine the rate of absorption of carbon dioxide by cement exposed to humid mixtures of carbon dioxide and air. The arrangement of the apparatus was the same as that employed in the preliminary experiments. The rates at which moist carbon dioxide and air passed through the apparatus were kept constant at about 3.5 litres per hour so that the atmospheric conditions above the exposed cement sample did not vary throughout the time of exposure. The cement was thoroughly stirred every morning and evening and samples were extracted, after thorough mixing, roughly every 24 hours. The results show that the amount of carbon dioxide absorbed is practically directly proportional to the time of exposure until a certain critical carbon dioxide content is attained. Beyond this critical point the rate of absorption is less and it remains constant at this lower value to the end of the experiment. The same applies also to the increase of the loss on ignition with exposure. The

carbon dioxide content at the critical point is constant for the one cement but is different for different cements, indicating that the activity of the cement towards moist carbon dioxide changes after the formation of a definite amount of carbonate. The amount of carbon dioxide at the critical point bears no relation to the amount of free lime present.

**CARBONATION AND TENSILE STRENGTH.**—In view of the difficulty of aerating large quantities of cement uniformly, the number of briquettes tested at each age was limited to three for each stage of aeration. The cements tested are described in Table 1.

The four cements exhibited the same general behaviour. For each cement the strength at early ages, e.g. 1 and 3 days, differ somewhat from those for the later ages, e.g. 7, 14 and 28 days. For the early ages the neat strength first decreases linearly with the degree of carbonation until a certain critical value of carbonate content is reached—this value is higher for the 3-day than for the one-day strength. Above this critical value aeration seems to have no further deleterious effect on strength until a second critical carbonate content is attained, after which the strength falls very rapidly to zero. The behaviour of the mortar strengths differs generally from that of the neat cement in two respects: (a) initially, with mortar specimens, increasing carbonation produces no appreciable effect on the mortar strength, (b) the mortar strengths persist to a higher degree of aeration than the neat strengths, i.e. the mortars develop strength after the cement has lost the power to develop strength in the neat state. The inflexion points observed with early age strengths indicate that the reaction between the cement, or its constituents, and carbon dioxide changes at these points.

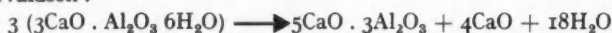
At 7 and 14 days the neat and mortar strengths decrease steadily with increasing degree of carbonation, except that the mortars exhibit the initial immunity observed with early strengths. For the 28-day strengths the initial phase of the reaction in which aeration appears to have little or no effect is present in both neat and mortar strengths—one case, cement "A," shows with mortars a definite increase as aeration proceeds.

From these results for specimens of standard consistency it is clear that the effect of a definite amount of carbonation depends upon the amount that had previously occurred. With a fresh cement comparatively small amounts may seriously affect the early strength without proving injurious to the later, e.g. 28-day, strengths.

**EFFECT OF CARBONATION ON HEAT OF HYDRATION.**—In view of the unexpected results obtained in the investigations of the rate of absorption of carbon dioxide and of the effect of carbonation on tensile strength, a method was sought which might yield some further information regarding the observed inflexion points. The method adopted was based on the fact that a marked heat effect is always observed when cement is mixed with water due to the hydration of its constituent compounds. It was thought, therefore, that a study of the heat evolved by cement and cement compounds, which had been previously exposed to various treatments, might supply useful information regarding the reactions taking place

during the mixing of cement. Since a number of compounds occurring in the cement clinker can be prepared in the pure state, these compounds were investigated as an introduction to the study of the more complex clinker.

The results suggested that unhydrated tricalcium aluminate is stable up to 1,000 deg. C. The same is not true of the hydrated sample. In this case there are two maxima, one at about 300 deg. and the other at about 700 deg. to 800 deg. C. It has been shown by previous investigators that tricalcium aluminate forms a stable hexahydrate which, on heating to about 300 deg. C., rapidly gives off water until the compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1.5 \text{H}_2\text{O}$  is formed. The increased heat effect between 200 and 300 deg. C. is therefore probably due to the dehydration of this hexahydrate. The fact that no increase is shown up to 200 deg. C. indicates that no decomposition of the hydrate occurs before this temperature is attained. This agrees with the results obtained by Thorvaldson, who found that heating at 200 deg. C. for 3 hours expelled less than 1 per cent. of the water, while 1 hour at 300 deg. C. expelled 75 per cent. of the total water of hydration. A further rise in ignition temperature to 400 deg. C. brings about a decrease in heat evolved. This may be due to the dehydration of part of the lower hydrate to the anhydrous material, which would probably have a lower rate of hydration resulting in a small heat evolution during the time of observation. In fact, it would be expected that the rate would finally approach that of the unhydrated tricalcium aluminate, i.e. 43 cal. per gram. Between 400 and 700 deg. C. the heat evolved increases rapidly with rise in temperature of ignition. This is thought to be due to the decomposition of the aluminate to a higher aluminate, probably pentacalcium trialuminate, according to the equation suggested by Thorvaldson :



Any such decomposition would liberate calcium oxide and, since the heat of hydration of CaO is very much greater than that of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , the heat evolved would increase with increasing decomposition of the aluminate. The decomposition reaches its maximum between 700 and 800 deg. C., while above this temperature, the equilibrium condition in the reaction moves towards the  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  side. This interpretation is in agreement with the results of Thorvaldson who found that the maximum decomposition occurred between 700 and 800 deg. C. Estimations of free lime on heated samples of hydrated tricalcium aluminate showed that decomposition with liberation of lime took place at 400 deg. C. This possibly accounts for the difference in heat obtained at 400 deg. C. for the hydrated as compared with the unhydrated sample.

Another factor which would influence the heat effect of the hydrated material between 200 and 800 deg. C. is the gradual increase in the percentage of tricalcium aluminate in the ignited samples in this range. The introduction of a correction for this factor would increase the heat per gram at these temperatures but would not materially change the form of the curve although it would accentuate the drop in heat effect between 300 and 400 deg. C.

When tricalcium silicate is brought into contact with a large excess of water the heat evolution is small but continues throughout the duration of the experi-



ment. For the unhydrated sample the results show that the heat evolved on hydration is practically independent of the temperature of ignition. This indicates that the tricalcium silicate in the unhydrated state undergoes no appreciable decomposition in the range 0 to 1,000 deg. C. Further, the total heat evolved in 40 minutes is very small, indicating that reaction between the sample and water takes place slowly.

The behaviour of the hydrated material is totally different. In this case the heat evolved gradually increases with increasing temperature. The more rapid increase between 400 and 500 deg. C. is probably due to the presence of some  $\text{Ca(OH)}_2$  formed by hydrolysis during the previous hydration. It was first thought that the continued increase in the heat evolved between 600 and 900 deg. C. might be due to the decomposition of some carbonate that had been formed during the storage of the samples in the desiccators. Analysis showed that the  $\text{CO}_2$  contents were far too low to account for the increased heat. It seems therefore that the increase is due to the partial decomposition of the silicate, this decomposition increasing with increasing temperature. This conclusion agrees with the results obtained by Carlson, who found that tricalcium silicate that has been exposed to moist air decomposes much more readily than when freshly burned. As Carlson concludes, the effect is probably due to the presence of free lime in the hydrated material. This is in agreement with the conclusions drawn by Bessey from his investigations on the effect of heat on cements. The data indicate that this decomposition sets in at temperatures below 700 deg. C.

The same method was applied to a typical example of an unhydrated normal Portland cement. For the calorimetric determinations 10 grams of cement were used with 100 c.c. of water. The results showed that, for the unhydrated cement, there is a greater increase in heat evolved in the ranges 200 to 300 deg. C. ; 400 to 500 deg. C. and 600 deg. C. upwards. The increase between 400 and 500 deg. C. is probably due to the decomposition of the  $\text{Ca(OH)}_2$  which is present to a certain extent in all unhydrated cements, and the rapid increase at temperatures above 600 deg. to the decomposition of calcium silicate and carbonate. The rise between 200 and 300 deg. C. seemed, on consideration of the curves for the pure compounds, to be due to the presence of tricalcium aluminate. In order to verify the presence of this aluminate, a hydrated sample of cement was investigated. The method of preparing this sample differed slightly from the procedure given for the pure compounds, as, in this case, the filtration was carried out in the presence of the carbon dioxide of the atmosphere and the dissolved material contained in the filtrate was not added to the sample. This was done in order to eliminate the masking effect of the  $\text{Ca(OH)}_2$  formed during the hydration on the aluminate curve above 350 deg. C. The maximum at 300 deg. C. found for the aluminate is now very pronounced, indicating the presence of this compound in the cement. There is a greater percentage drop in heat effect between 400 and 300 deg. C. in the case of Portland cement than in tricalcium aluminate. This is probably due to the fact that the conditions of the experiment are different. In the cement the free lime formed is removed, while any decomposition of tricalcium aluminate

which sets in at 400 deg. C. will tend to decrease the drop between 300 and 400 deg. C.

As carbon dioxide in the presence of water vapour decomposes certain constituents of cement and, since the strength is markedly changed, it can be assumed that either tricalcium aluminate or tricalcium silicate or both are attacked. If this is the case, the heat of hydration/temperature of ignition curve of a cement should alter as aeration proceeds. A preliminary examination was carried out by determining the heat evolved after igniting at a temperature of 300 deg. C. This temperature was selected because, in the presence of hydrated material, the heat evolved by cement ignited at this temperature is probably largely due to tricalcium aluminate and any change in this constituent would thus be seen. The results are somewhat irregular, but the heat evolved gradually increases to a maximum as carbonation proceeds and then suddenly falls to a very low value. Beyond this critical point the heat changes only very slowly with aeration. The cause of the gradual increase in the quantity of heat evolved is not quite clear but it may possibly be due to an increased activity of some of the constituents due to the decrease of particle size produced by aeration and also to the splitting up of the conglomerates in the cement, thus setting free active material; in other words the availability of certain constituents for hydration may be increased.

In general, the hydraulic properties of Portland cement are presumed to be due to the presence of the calcium aluminates and silicates, tricalcium aluminate, tricalcium silicate and dicalcium silicate; for the purposes of this discussion the tetracalcium aluminoferrite present is considered to behave towards aeration like tricalcium aluminate. Since the longest period of maturing specimens for strength determinations has been 28 days it may be assumed that the chief constituents responsible for the development of strength are tricalcium silicate and tricalcium aluminate. The variations in the behaviour of the cement during aeration may thus be attributed to the action of carbon dioxide and moisture on these two constituents. Anderegg and Hubbell found that the degree of hydration—for particles of  $25\ \mu$ —attained with tricalcium aluminate in 3 hours was equivalent to that attained with tricalcium silicate in 7 days and to that with dicalcium silicate in  $5\frac{1}{2}$  months. If, therefore, it is assumed that these two constituents retain their relative activity in the cement, it would be expected that the tricalcium aluminate would be attacked in preference to the tricalcium silicate. That this is actually the case seems to be corroborated by the fact that in each cement the rate of absorption of carbon dioxide changes at a definite stage of aeration. These considerations suggest that the main reaction taking place during early aeration is the decomposition of the tricalcium aluminate, while during the later stages it involves chiefly the tricalcium silicate. The most unexpected feature of the results is the sudden drop which is observed. It might be expected that the heat would gradually decrease with aeration, as would undoubtedly be the case if the heat of complete hydration was measured. However, the drop corresponds to 11 cal./g. which is equivalent to about 5 per cent.  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  assuming the heat of hydration of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  to be

214 cal./g. For complete decomposition this will take up 2.5 per cent.  $\text{CO}_2$ . This means that a drop of 11 cal./g. could take place over a range of 2.5 per cent.  $\text{CO}_2$ , which is of the order found.

The most striking conclusion reached is, that for early ages, the tricalcium aluminate exercises a predominant influence on the tensile strengths of both neat and mortar specimens, while at later ages, viz. 28 days, this same constituent exercises little or no influence—in fact it may even be detrimental to the strength. Other investigators have come to the similar conclusion that tricalcium aluminate can influence the early strength very appreciably.

For the early ages, beyond the inflexion point, the strength is, within certain limits, independent of aeration. If the foregoing deductions be true this means that a reduction in the tricalcium silicate content does not effect the strength in this region. This may perhaps be due to the rate of hydration. If this is low, only a fraction of the tricalcium silicate will hydrate during these periods and an appreciable amount of unhydrated material will remain. Although aeration reduces the quantity of tricalcium silicate it is not necessary to assume that corresponding reductions in the rates of development of strength must occur until the percentage remaining reaches a certain minimum value. As soon as this value has been reached, further aeration will again reduce the strength. This period of insensitivity to aeration is not shown by the strength results at later ages. At these ages it is generally found that it is the initial aeration which produces little effect on the strength. This implies on the above hypothesis that the removal of tricalcium aluminate has no positive effect on the strength at these ages. The data at present available may not be sufficient to prove whether these deductions are true or not, but the investigation shows conclusively that the possibility of the importance of tricalcium aluminate to the strength of Portland cement at early ages should not be overlooked in investigations concerning the hydraulic properties of these cements.

In the present investigation of the effect of carbonation on setting time, aeration was effected by exposing the cement to an atmosphere of moist carbon dioxide and the state of aeration of the cement was ascertained by the determination of its carbonate content. The setting times were determined throughout by the Vicat needle method.

The results show that the influence of aeration on the setting time of cement is not unidirectional. Samples of widely differing degrees of aeration may exhibit the same setting time, while two samples exposed to the atmosphere for nearly the same time may differ considerably in setting time. At high carbonate content the cements invariably develop a short, in fact very nearly a flash, set. At this point the setting time remains fairly constant over a small range of carbonate content and then increases to a very long set of over 24 hours initial setting time which is probably permanent. The data when plotted diagrammatically show a series of maxima and minima. Repeated experiments proved that these variations were not quantitatively reproducible, i.e. two samples treated identically would both show a series of maxima and minima but these would

not necessarily take place at the same carbon dioxide content. In other words, the  $\text{CO}_2$  content at which a short or a long set would occur would not be constant from sample to sample of the same cement. In all cases, however, the final flash set developed immediately before the complete loss of the early neat tensile strength. It was thought that these variations might possibly be due either to the varying water content necessary to give normal consistency or to the difficulty of obtaining concordant results in the setting times due to fluctuations in external conditions during measurement. In order to investigate the reality of these fluctuations in setting time it was necessary to test both these possibilities. For this purpose samples were tested at both constant water content and at normal consistence. For testing the reproducibility of the measurements, setting times were determined on samples (of a definite degree of aeration) at intervals of 24 hours.

The setting time values show very little variation from day to day, indicating that the fluctuations are not due to experimental variations. Further the values for the samples of constant water content also show fluctuations of the same order as the normal consistence samples. It is thus clear that the cause of these fluctuations is of a more fundamental character than water content variations or determination errors. When water—in a limited amount—and cement clinker are brought together in the normal way for making cement pastes, the velocity of the reaction taking place depends primarily upon the affinity of the cement constituents for water. If this affinity is great it would be expected that the time of setting would be short, while on the other hand, with a weak affinity, that the setting time would be long. Yet, although this affinity is the primary cause, the setting time can be greatly influenced by at least two other factors, namely, the size of the particle and the presence or absence of impurities over the particle surface. Both these factors are affected by aeration in atmospheres of moist carbon dioxide. When the cement is exposed to such atmospheres the particles are attacked and calcium carbonate is formed. If the carbonate is formed as a film over the surface of the particles, it will decrease their activity and so tend to prolong the setting time. On further aeration there will be a gradual penetration of moisture through the carbonate film with the consequent hydration or hydrolysis of some of the active core. The subsequent volume changes will break off the inert film thus exposing an active surface and reducing the particle size. This would tend to quicken the set.

In view of these possible explanations some experiments were made to test whether the set obtained after aeration could be influenced by mechanical means. The first series of experiments was carried out as follows: A sample (of a definite degree of aeration) was divided into two portions. One was tested at normal consistency, the other was gently rubbed in a metal mortar using a soft rubber pestle—in this way the surface coating if present should be partially broken up, while no actual grinding of the particles took place. After this treatment the setting time was determined, again at normal consistency. Several samples of widely different states of aeration were tested in this way. It is evident from

the results that gentle rubbing with a soft rubber pestle can exercise an appreciable influence on the setting time of the cement. With long setting times there is a very pronounced acceleration, while with short sets the effect is not so marked although the tendency is in the same direction. Rubbing in this manner also affects the water content necessary for normal consistency. The decrease in setting time produced by the rubbing depends upon the length of time taken and upon the pressure applied during the process. The results are therefore only qualitative.

Another series of experiments was carried out as follows: Cement, of a definite degree of aeration, was stored in a stoppered bottle and at intervals of 7, 14, 28 and 42 days the setting time of a typical specimen was taken after thoroughly shaking the bottle to ensure good sampling. A series of these tests was carried out, the water content of the tested part being maintained constant throughout any one series. The results show that cement samples of medium or quick set undergo no change by the type of storage described, while, on the other hand samples of slow set exhibit a strong tendency to develop quicker sets. With the slow sets the surfaces of the cement particles are largely coated with inert material formed during aeration, and probably during storage flaking of this layer occurs with consequent acceleration of the set. The results are in agreement with the suggestion that the variation in the setting time obtained during aeration of cement is due to the complete or partial coating of the surface of the active particles with a film of inert material, probably calcium carbonate, and subsequent flaking of this inert film. Further investigation is, however, required.

It has generally been tacitly assumed that the aggregate used in cement mortars and concrete only plays the part of an inert filler and that the strength is due entirely to the cement. It has already been noted that, when the carbonation of a cement has reached a sufficiently advanced stage, a cement was produced of which neat mixes developed no strength at early ages—in fact in some instances the briquettes had no strength up to about 30 days though they gradually hardened, but which, when diluted with sand (e.g. 1 : 3 mortar by weight) could develop quite appreciable strength in 24 hours. In view of this result the problem of the behaviour of the aggregate was investigated. For this purpose a sample of the rapid-hardening Portland cement was exposed in drums to the action of carbon dioxide and moisture. The exposure was continued until the  $\text{CO}_2$  content reached a value of 15.06 per cent., when the loss on ignition was 19.56 per cent. At this stage, the apparent initial setting time of the cement was about 48 hours. The neat briquettes developed no strength at 7 days at normal consistency, while under the same conditions the 1 : 3 (by weight) sand mortar gave a strength of 105 lb. per square inch at 1 day and 209 lb. per square inch at 7 days.

When this remarkable behaviour was first observed it was thought that the mortar strength might be due to the higher water-cement-ratio in these mixes as compared with the neat cement specimens. In order to test this hypothesis two series of neat and mortar tests were made in which the mortars were mixed with 25 per cent. of the water used for the neat samples. The range of water

content varied from a very dry to a wet mix. With the driest mortar (7.5 per cent. water) great difficulty was experienced in filling the moulds. Naturally, owing to a slight absorption of water by the sand, there is less water available in the mortars than in the corresponding neat specimens. The strength values obtained in these tests show that the higher water-cement-ratio was not the cause of development of strength in the mortars.

As the carbonation of the unhydrated cement proceeds the active cement particles are steadily reduced in diameter until finally some of the original smaller particles have been completely decomposed. The direct consequence of this would be an increase in the average distance between adjacent active cement particles. Ultimately the stage would be reached when the active particles were so thinly distributed in the cement mass that, both during and after hydration, no continuous connection can be made between the particles to form a structure and consequently no strength can result. This was assumed to be the state of the cement when no early-age neat tensile strength was obtained. If such a cement were mixed with sand the fine cement particles would be distributed over the surface of the aggregate particles and these latter, if large enough, would then act as links between the various active particles. For the experimental verification of this theory two series of tests were made with silica sand and other aggregates.

The results show that the strength does not attain measurable dimensions until a certain size of aggregate is used for the mortars. After this value is attained the strength first rapidly increases to a maximum and then gradually decreases with increasing size of aggregate. This latter tendency may either be due to differences in packing or may be explained as follows: The maximum strength possible would be obtained when all the active cement particles are connected together by means of the aggregate. This, of course, is experimentally impossible due to the fact that some cement particles are located in the pore spaces between the aggregate particles, and are of such distance from the surfaces of the latter, that they are ineffective for development of strength. As the radius of the sand particles increases so do the individual pore spaces increase in size. If, therefore, it is assumed that the active cement particles are uniformly distributed, it will be seen that when the pore spaces increase, the number of active cement particles isolated in these spaces will also increase. The consequence is that a smaller number of active cement particles is available to give strength, thus giving rise to a decrease in strength with increasing radius of aggregate.

In order to test the variation of strength with the concentration of aggregate particles of a definite size, the only practical method possible is to vary the cement-sand-ratio. The results show that for low concentrations of sand particles the strength developed is very small. When the concentration has been increased sufficiently to give strength, then further increases have a beneficial effect on the strength until a maximum value is reached, after which the strength shows a tendency to fall off with increasing sand-cement-ratio.

These effects can be explained on the basis of the above theory as follows:



Before any strength can be developed by the mortar it is essential that a certain minimum number of active cement particles be so connected together as to give the whole mass a definite rigid structure. This will entail the presence of a certain minimum concentration of aggregate.

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## Abstracts from the Foreign Press.

**Relations between Chemical Composition, Methods of Production, and Quality of Portland Cements.** By D. Steiner. (*Zement*, 1935, pp. 469, 490.)—A normal commercial cement slurry was used as the basis of a series of investigations on the quality of Portland cements of varying compositions made by different methods. So long as good burning was obtained there was only a very small improvement in quality due to finer grinding of the raw material (e.g., increasing fineness from 10½ per cent. to 1 per cent. residue on the 4,900-mesh sieve).

The quality of a cement was based on the sum of the tensile or compressive strengths at 1, 2, 3, 7 and 28 days. Using this figure, it was found that for silica ratios 3.3 and 2.7 the quality improved with the  $3\text{CaO}.\text{SiO}_2$  content. In the group with silica ratio 2.0 this is also observed, but for clinkers containing free CaO there is a drop in quality. In the group with silica ratio 1.4 the curve is irregular and there is usually a tendency to unsoundness. Similar results were obtained when the iron content was increased, showing that compounds other than  $3\text{CaO}.\text{SiO}_2$  play a subordinate part. For the groups with silica moduli 3.3, 2.7, and 2.0 the increase in strength due to the  $3\text{CaO}.\text{SiO}_2$  is increased with rising  $3\text{CaO}.\text{Al}_2\text{O}_3$  content. In the group with silica modulus 1.4, on the other hand, there is a decrease in strength due to the greater free lime content. The rise in strength due to brownmillerite is not due to its own strength properties, but because it acts as a flux and helps in the formation of the other clinker constituents. Hence a certain content of brownmillerite is required for good burning, but if this amount is exceeded there is a decrease in strength. A possible solution is to use another flux (for instance, fluorspar) in order to limit the amount of brownmillerite.  $2\text{CaO}.\text{Fe}_2\text{O}_3$  acts in the same way for high-iron cements as  $3\text{CaO}.\text{Al}_2\text{O}_3$  does for low-iron cements.

Curves are given by which the approximate strength of a cement tested under fixed conditions can be calculated from the chemical composition. The strength of clinker rises almost proportionally with its  $3\text{CaO}.\text{SiO}_2$  content. The best strength, however, is not obtained with pure  $3\text{CaO}.\text{SiO}_2$  but when there is 10 to 15 per cent.  $3\text{CaO}.\text{Al}_2\text{O}_3$  present, the lowest possible amount of brownmillerite, and no  $2\text{CaO}.\text{SiO}_2$ .

With lower ratios of compressive to tensile strength there is less tendency to shrinkage. It has been found that with increasing lime content the com-

pressive strength increases either very little or not at all, but there is an increase in tensile strength. This should be kept in mind in the production of high-quality cements. The ratio of compressive to tensile strength improves with increasing silica modulus. In all cases this ratio rises with age, showing that the greater part of the tensile strength is obtained at an early date. The ratio decreases with increasing water content.

All the cements were ground to 7 per cent. residue on the 4,900-mesh sieve, and 5 per cent. gypsum was used as a retarder.

**Air Content of Plastic Mortars.** By W. Czernin. (*Tonind. Zeit.*, 1936, p. 336.)—Tests have been carried out by the author to determine the amount of air included in a specimen during gauging. A cylindrical vessel was filled with mortar, the volume noted, and water added up to a fixed mark. The vessel was then gently agitated to mix the mortar and water so that the entrained air bubbles could be released. If, after this treatment, it is found that the level of the water is lower, fresh water is added to bring the level back to the mark. Agitation and addition of water are continued until there is no further change. From the volume of the water added the volume of the entrained air can be calculated. This test is claimed to be superior to the usual method which makes use of the specific gravity of the set cement, because the latter is not known accurately. Values for entrained air varied from 2.8 per cent. to 13.2 per cent. in the tests. It was found that least air was entrained when a sand was used which had missing grades. The addition of 0.1 per cent. of a water-repellent material increased the air voids from 6.45 to 13.2 per cent.

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